I, the undersigned, who have prepared English translation which is attached herewith, hereby declare that the aforementioned translation is true and correct translation of officially certified copy of the Korean Patent Application No. 10-2002-0035793 filed on June 25, 2002.

Translator: Kim, EunJeong
KIM, Eun-Jeong

Date: February 11, 2008

KOREAN INTELLECTUAL PROPERTY OFFICE

This is to certify that the following application annexed hereto is a true copy form the records of the Korean Intellectual Property Office.

Date of Application:	June 25, 2002
Application Number:	Patent Application No. 10-2002-0035793
Applicant(s)	Micro Science Tech Co., Ltd.

COMMISSIONER

APPLICATION FOR PATENT

To the Commissioner of
the Korean Intellectual Property Office

FILING DATE: June 25, 2002

TITLE: ANTI-MICROBIAL POLYMER RESIN COMPOSITE

APPLICANT Micro Science Tech Co., Ltd.
447-6 Wangrim-ri, Bongdam-eup, Hwaseong-city, Gyeonggi-do 445-895, Republic of Korea

ATTORNEYS: Hwang inam

INVENTOR MOON, Woong-Sig
201-1402 LG village, 530 Geumgok-dong, Gwonseon-gu, Suwon-city, Gyeonggi-do 441-842, Republic of Korea

KIM, Jae-Chul
102-1005 Samik 1-cha apt., 241 Geumgok-dong, Gwonseon-gu, Suwon-city, Gyeonggi-do 441-840, Republic of Korea

CHUNG, Kyoo-Hyun
109-701 Muakhyundai apt., Muak-dong, Jongro-gu, Seoul 110-797, Republic of Korea

KONG, Ki-Oh
105-602 Geonyoung apt., Arm-maeul, Imae-dong, Bundang-gu, Seongnam-city 463-060, Republic of Korea

KIM, Jung Chul
414-9 F-dong, Wangrim art villa, Wangrim-ri, Bongdam-eup, Hwaseong-city, Gyeonggi-do 445-895, Republic of Korea

KANG, Heun-Soo
707-101 Hwaseong village, MoKreyon-maeul, Yatap-dong, Bundang-gu, Seongnam-city 463-070, Republic of Korea

Submitted herewith is an application identified above pursuant to Article 42 of the Patent Act.

【ABSTRACT OF THE DISCLOSURE】

【ABSTRACT】

The present invention relates to an anti-microbial polymer resin composition, the present invention discloses an anti-microbial polymer resin composition comprising at least one material selected from a group consisting of an anti-microbial agent selected from a group consisting of ciprofloxacin, grepafloxacin, lemefloxacin, norfloxacin, pipemidic acid, sparfloxacin, temafloxacin and tosufloxacin; and an anti-fungal/ anti-pollutant agent selected from a group consisting of ketoconazole, fluconazole, itraconazole, econazole, miconazole, iconazole as effective components.

The anti-microbial polymer resin composition of the present invention is safe to a human body, and maintains superior anti-microbial effects even after molding, and can solve the problem of toxicity by elution,. Therefore, the present invention can be extensively applied for major material, industrial articles, living articles, anti-contaminating paint of medical fields.

【SPECIFICATION】

【TITLE OF THE INVENTION】

ANTI-MICROBIAL POLYMER RESIN COMPOSITE

【DETAILED DESCRIPTION OF THE INVENTION】

【OBJECT OF THE INVENTION】

【FILED OF THE INVENTION AND DESCRIPTION OF THE RELATED ART】

The present invention relates to an anti-microbial polymer resin composite(i.e., composition). More particularly, the present invention relates to an anti-microbial polymer resin composition applying an anti-microbial material, that is safe to a human body, has superior combination property with materials for commonly used polymer and medical materials, and has superior anti-microbial property, to various matter, so as to have superior an anti-microbial effects even after molding, and to solve the problem of toxicity by elution.

Various forms of organic anti-microbial formulations for conventional anti-microbial and anti-pollutant functions such as quaternary ammonium salt, chlorohexidine, carbendazim, thiazole, azole, Sn types, etc. have been reported. However, many of the anti-microbial and anti-pollutant products using the above materials have problems including unsecured safety due to toxicity, and ecosystem destruction due to release of environmental hormones. Additionally, their anti-microbial effects may be decreased due to thermal decomposition during high temperature processing, and product deterioration due to yellowing may also occur. Particularly, a polymer resin used in the medical field such as for an artificial blood vessel, an artificial heart, an artificial bone, artificial skin, etc. should be secured safety to a human body, and they should be protected from various pathogenic bacteria. However, anti-microbial materials of the prior art cannot

completely satisfy these requirements.

【TECHNICAL SOLUTION TO BE SOLVED THE INVENTION】

In order to solve these problems of the prior art, it is an object of the present invention to provide a new anti-microbial polymer resin composition that has superior combination property and compatibility with a polymer resin, exhibits superior anti-microbial effects even after molding processing, and can solve the problem of toxicity due to an elution, and thus can be extensively used for a medical polymer resin, natural rubber, petrochemical product and the like by using an anti-microbial material, of which safety to a human body is secured.

【CONSTITUTIONS OF THE INVENTION】

The anti-microbial polymer resin composition of the present invention comprises at least one material selected from a group consisting of an anti-microbial agent selected from a group consisting of ciprofloxacin, grepafloxacin, lemefloxacin, norfloxacin, pipemidic acid, sparfloxacin, temafloxacin and tosufloxacin; and an anti-fungal/ anti-pollutant agent selected from a group consisting of ketoconazole, fluconazole, itraconazole, econazole, miconazole, iconazole as effective components.

As the anti-microbial agent, materials known to be safe to a human body can be used. The anti-microbial agent is preferably contained in the anti-microbial polymer resin of the present invention in an amount of 0.1 to 30 wt% based on the total composition. If the content of the anti-microbial agent is less than 0.1 wt%, the anti-microbial effect is slight, and if it exceeds 30 wt%, the improvement effect is not significant thus making it uneconomical.

As the anti-fungi agents, materials known to be safe to a human body can be used, the present invention confirmed that materials have an anti-pollutant property. The anti-fungi/ anti-pollutant agent is preferably contained in the polymer resin of the present invention in an amount of 0.1 to 30 wt% based on the total composition. If the content is less than 0.1 wt%, the anti-fungi effect is slight, and if it exceeds 30 wt%, the improvement effect is not significant thus making it uneconomical.

If the anti-microbial and anti-fungi/anti-pollutant agent (hereinafter, "anti-microbial materials) is mixed, it can be expected an anti-fungi, and anti-pollution effects.

The common polymer resin combined with the anti-microbial materials comprises a liquid-phase polymer resin (hereinafter, liquid-phase resin) and a solid polymer resin (wherein, when an external form of the polymer is gel type, it also regards as the solid).

The present invention also comprises the anti-microbial master batch (M/B) composition comprising at least one materials selected from the group consisting of anti-microbial and anti-fungi/anti-pollutant agent as effective components.

The liquid-phase resin is alkyd resin, acryl resin, urethane resin, epoxy resin, phenol resin, urea resin, melamine resin, and a modified resin thereof, hydroxypropylacrylate, 1,6-hexanedioldiacrylate, pentaerythritoltriacrylate, polyethylenedipentaerythritol and the like, at least one of the materials can combine with the anti-microbial materials.

According to the anti-microbial composition of the present invention, commonly used additives such as a pigment, a diluent, a physical property

controlling monomer and oligomer, a polyol (e.g., acryl polyol, urethane polyol, epoxy polyol, urea-melamine polyol, etc.), etc. can be further added to the liquid resin composition. As the physical property controlling monomer, one or more kinds selected from a group consisting of hydroxypropylacrylate (HPA), 1,6-hexandioldiacrylate (HDDA), pentaerythritol triacrylate (PETA), polyethylenglycoldiacrylate (PEGDA), trimethylolpropane ethoxylate triacrylate (TMPEOTA), and dipentaerythritol hexaacrylate (DPHA) can be used.

The anti-microbial and commonly used resin composition can be used as a coating agent, and natural curing, heat-curing, UV curing treatment, etc. can be involved.

As the solid polymer resin, Linear low density polyethylene(LLDPE), low density polyethylene(LDPE), high density polyethylene(HDPE), polypropylene (PP), polyvinylchloride (PVC), ABS(acrylonitrile-butadiene-styrene), SAN(Styrene Acrylonitrile), polycarbonate (PC), polystyrene (PS), polyvinylalcohol (PVA), polyacrylonitrile, polybutadiene, polyacrylic acid, polyacrylimide, polysulfone, polyacetal, polyamide-imide, polytetrafluoroethylene, polyneoprene, polydimethylsiloxane, polymethylmethacrylate, polyetheretherketone, polyphenylenesulfide, polyvinylfluoride, polyvinylacetate, polyetherimide, polyvinylidinefluoride, polyethersulfone, polyurethane, silicon resin, and natural rubber can be used, at least one of the materials can be combined with the anti-microbial materials.

In addition, the polymer resin composition of the present invention may further comprise at least one additives selected from a group consisting of an antioxidant, a heat-stabilizer, and a dispersant, which are commonly used in plastic molding processing.

The antioxidant is used for preventing and inhibiting product deterioration such as discoloration due to oxygen in the air. Examples thereof include 2,6-di-tert-butyl-p-cresol, n-octadecyl-3-(4-hydroxy-3m5-ditert-butylphenyl)propionate, tetrabis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, 1,3,5-trimethyl-2,4,6-tris-(3,5-di-t-butyl-4-hydroxybenzene)benzene, etc. The content of the antioxidant is preferably 0.1 to 2.5 wt% of the total composition. If the content is less than 0.1 wt%, the anti-oxidation effect is slight, and if it exceeds 2.5 wt%, a further effect improvement cannot be expected.

The heat-stabilizer is used for aiding maintenance of physical and chemical properties of the resin during usage of the final product, and prevention of thermal degeneration during processing. As the heat-stabilizer, zinc stearate [$Zn(C_{17}H_{35}COO)_2$], magnesium stearate [$Mg(C_{17}H_{35}COO)_2$], barium stearate [$Ba(C_{17}H_{35}COO)_2$], etc. can be used. The content of the heat stabilizer is preferably 0.1 to 3.5 wt% of the total composition. If the content is less than 0.1 wt%, the heat stabilizing effect is slight, and if it exceeds 3.5 wt%, a further effect improvement cannot be expected.

The dispersant functions for uniformly dispersing commonly used resin and pharmaceutically active material. The examples include N,N'-ethylene-bis-stearamide (E.B.S.), low density polyethylene wax, etc., and they can be used alone or in combination. The content of the dispersant is preferably 0.1 to 15 wt% of the total composition. If the content is less than 0.1 wt%, dispersion is slight, and if it exceeds 15 wt%, a further effect improvement cannot be expected.

In the present invention, the master batch can be used as a high functional additive in processing of industrial appliances such as food packaging material, plastic, etc., and the added amount is preferably 0.5 to 30 wt%.

In addition, according to the present invention, a medical instrument/appliance can be prepared by applying the anti-microbial materials to the medical polymer resin. The medical polymer resin is preferably selected from a group consisting of polyethylene (PE), polypropylene (PP), polycarbonate (PC), polyvinylchloride (PVC), polystyrene (PS), epoxy resin, polytetrafluoroethylene (PTFE), polyacetal (POM), polyamide (PA), polyurethane (PU), ethylene-vinylacetate copolymer (EVA), polymethylmethacrylate (PMMA), polyvinylalcohol (PVA), polycaprolactone (PCL), and a copolymer thereof; silicon resin; natural rubber; and a synthetic rubber. The content of the anti-microbial material is preferably 0.1 to 10 wt% of the total composition. If the content is less than 0.1 wt%, the anti-microbial effect is slight, and if it exceeds 10 wt%, a further effect improvement cannot be expected.

The present invention will be explained with reference to the following Examples, but they are to illustrate the present invention and the present invention is not limited to them.

<Example 1> Preparation of anti-microbial liquid polymer resin compositions

One or two kinds of the anti-microbials ciprofloxacine and norfloxacin, and the anti-fungi/anti-pollutants ketoconazole and fluconazole, were finely powdered. The anti-microbials were slowly introduced into a mixer containing a liquid phase resin at room temperature while stirring at a high speed to uniformly mix them to prepare a liquid anti-microbial resin composition with the compositions of Table 21 (composition of 100 wt%).

[Table 1] Anti-microbial liquid polymer resin compositions

Anti-microbial	Epoxy resin[3)]	Urethane-acrylate reisn[4)]	Acryl-melamine resin[5)]	Alkyd-melamine resin[6)]	Acrylpolyol resin[7)]
Ciprofloxacin[1)]	99	99	99	99	99
Norfloxacin[2)]	99	99	99	99	99
Ketoconazole[8)]	99.5	99.5	99.5	99.5	99.5
Norfloxacin+fluconazole[9)]	98.5	98.5	98.5	98.5	98.5
Ciprofloxacin+ketoconazole[10)]	98.5	98.5	98.5	98.5	98.5

Note)

1) addition: 1 wt%, 2) addition: 1 wt%,

3) Samwha paint industry Co. Ltd., product SB-EE-400

4) Samwha paint industry Co. Ltd., product SB-V-100

5) Samwha paint industry Co. Ltd., product SB-MA-61

6) Samwha paint industry Co. Ltd., product SB-MA-20

7) Aekyung Chemical Co. Ltd., product BURNOK

8) 0.5 wt% of Ketoconazole

9) 1 wt% of Norfloxacin + 0.5 wt% of fluconazole

10) 1 wt% of Ciprofloxacin + 0.5 wt% of ketoconazole 0.5

<Experiment 1> Anti-microbial, anti-pollution and yellowing tests for anti-microbial liquid polymer resin

The anti-microbial liquid resins prepared in Examples 12 were respectively coated on a polyethylene sheet and an aluminum plate, and then each of them was naturally cured, thermally cured, or UV-cured. Anti-microbial, anti-

pollution, and yellowing tests were conducted, and the results are as described in Table 2.

[Table 2] Curing conditions and anti-microbial, yellowing, and anti-pollution test results

	Composition 1[1]	Composition 2[2]	Composition 3[3]	Composition 4[4]
Curing method	natural	thermal	UV	natural
Drying condition	2 hrs (20□)	30 min. (150□160 □)	8m/min (high pressure mercury lamp 80W/cm 1 Lamp)	2 hrs (20 □)
Thickness of dried film (μm)	40	40	20	40
Anti-fungi property[5]	4 grade	4 grade	4 grade	0 grade
Anti-microbial property[6]	7	8.0	7.5	7
Yellowing [7]	pass	pass	pass	pass
Anti-polluting property [8]	-	-	pass	pass

Note)

1) 1wt% of ciprofloxacin + 99wt% of epoxy resin

2) 1wt% of ciprofloxacin + 99wt% of (acryl + melamine resin)

3) 1wt% of norfloxacin + 0.5 wt% of fluconazole + 98.5 wt% of (urethane + acrylate resin)

4) 1 wt% of ciprofloxacin + 0.5 wt% of ketoconazole + 98.5 wt% of epoxy resin 98.5

5) strain : P. citrinum KCTC 6990 (measured by ASTM G21)

Grade : 0 grade – No mold growth on a sample

1 grade – Mold grew within 10% on a sample

2 grade – Mold grew 10 to 30 % on a sample

3 grade – Mold grew 30 to 60 % on a sample.

4 grade – Mold grew 60 % or more on a sample.

6) strain and test method : E.coli, KCTC 1682 (ASTM G22 method)

7) yellowing test: measured by ASTM D1925

8) Anti-pollution test: measured by ASTM D5589

<Example 2> Preparation of anti-microbial polymer resins and anti-microbial tests

As an anti-microbial agent, ciprofloxacin and norfloxacin were added to and mixed with a commonly used resin with the composition as shown in the following Table 3, and zinc stearate as a heat stabilizer and paraffin wax and E.B.S. as a dispersant were added and all compounds were mixed in a high speed mixer. The composition was manufactured into a sample of a size of 4.5 x 7.0 cm while changing the temperature from 100 to 300 □ using a preexisting injection molding apparatus. The anti-microbial effect was confirmed by ASTM G22.

[Table 3] Antimicrobial polymer resin composition and antimicrobial test results[1]

		PP	LLDPE	LDPE	HDPE	ABS	SAN
Cipro-floxacin	5 (wt%)	95	95	95	95	95	95
	Inhibition zone[2]	8.5±1	9.5±1	9.5±1	9.0±1	8.5±1	8.5±1
	3 (wt%)	97	97	97	97	97	97
	Inhibition zone	8.0±1	9.0±1	8.5±1	9.0±1	8.5±1	8.5±1

	1 (wt%)	99	99	99	99	99	99
	Inhibition zone	6.0±1	7.0±1	6.5±1	6.0±1	6.0±1	6.0±1
Nor-floxacin	5 (wt%)	95	95	95	95	95	95
	Inhibition zone	7.5±1	8.0±1	8.0±1	7.5±1	7.5±1	7.5±1
	3 (wt%)	97	97	97	97	97	97
	Inhibition zone	6.5±1	7.5±1	7.5±1	6.5±1	6.5±1	6.5±
	1(wt%)	99	99	99	99	99	99
	Inhibition zone	4±1	4.5±1	4.0±1	4.0±1	3.5±1	4.0±1

Note) Each commonly used resin (PP, LLDPE, LDPE, HDPE, ABS, SAN) comprised 0.2 wt% of zinc stearate, 0.2 wt% of paraffin wax and 0.25 wt% of E.B.S.

1) ASTM G22 method, host: *E.coli* (KCTC 1682)

2) Inhibition zone, unit: mm

<Example 3> Preparation of anti-microbial master batches and anti-microbial tests

A ciprofloxacin as known anti-microbial, a commercialized commonly used LLDPE resin, a dispersant, and an antioxidant were introduced into a high speed mixer, they were stirred at a high speed for about 30 minutes to mix, and then extrusion molded in an extrusion molding apparatus at a molding temperature of 170 to 190 ℃ to prepare an anti-microbial master batch in a pellet form. Each anti-microbial master batch was prepared by using HDPE and PP by the same method. Each compositional ratio is as shown in Table 4. Anti-microbial tests results are described in Table 5.

[Table 4] Composition of anti-microbial master batches

	LLDPE[1)]	HDPE[2)]	PP[3)]	4)	Dispersant /lubricant[5)]	Antioxidant[6)]	Dispersant[7)]	Total (wt%)
Composition1	75.9	-	-	10	2	0.1	10	100
Compostion2	-	73.9	-	10	2	0.1	10	100
Composition3	-	-	75.44	10	1.5	0.1	10	100

Note) 1) SK Co. Ltd. Product name CA 110

2) SK Co. Ltd. Product name JH 910

3) product name H360F 4) Ciprofloxacin

5) N,N'-ethylene bis stearamide (E.B.S)

6) n-octadecyl-3(3‘-5’-di-t-butyl-4-hydroxyphenyl)propionate

7) polyethylene wax

[Table 5] Anti-microbial testfor anti-microbial master batches[1)]

	E. coli (KCTC 1682)	S. aureus (KCTC 1621)	S. typhimurium (KCTC 1925)	P. aeruginosa (KCTC 2004)
Composition 1	9.5mm±1mm	9mm±1mm	14mm±1mm	10mm±1mm
Composition 2	9mm±1mm	10mm±1mm	12mm±1mm	9mm±1mm
Composition 3	10mm±1mm	10mm±1mm	13mm±1mm	9mm±1mm

1) ASTM G22 method

<Example 4> Preparation of anti-microbial master batches

Anti-microbial master batches with the compositions as shown in Table 6 were prepared by finely powdering one or two components of ciprofloxacin, pipemidic acid, ketoconazole and fluconazole, by the same method as in Example 3, and anti-microbial tests were conducted. The results are as described in Table 7. As a dispersant, N,N'-ethylene bis stearamide (E.B.S.) and polyethylene wax were used, and as an antioxidant, n-octadecyl-3(3'5'-di-t-butyl-4-hydroxyphenyl)propionate) was used.

[Table 6] Compositions of anti-microbial master batches

	LLDPE	Ciprofloxacin	Pipemidic acid	ketoconazole	fluconazole	Dispersant/lubricant	Anti-oxidant	Dispersant	Total (wt%)
Composition 1	84.9	1	-	2	-	2	0.1	10	100
Composition 2	84.9	1	-	-	2	2	0.1	10	100
Composition 3	82.2	-	1	2	-	1.5	0.3	13	100
Composition 4	82.2	-	1	-	2	1.5	0.3	13	100

[Table 7] Anti-microbial test for anti-microbial master batch

	Strain	Composition 1	Composition 2	Composition 3	Composition 4
Anti-microbial 1) (Inhibition zone)	E.coli(KCTC 1682)	8mm±1mm	9mm±1mm	8mm±1mm	10mm±1mm
	S.typhimurium (KCTC 1925)	11mm±1mm	11mm±1mm	10mm±1mm	10mm±1mm
	S. aureus (KCTC 1621)	9mm±1mm	8mm±1mm	8mm±1mm	7mm±1mm
Anti-	C. albicans (KCTC 7729)	0 grade	0 grade	0 grade	0 grade

fungi[2]	A. flavus (KCTC 6961)	0 grade	0 grade	0 grade	0 grade
Anti-pollutant[3]		Pass	pass	pass	Pass

Note) 1) measured by ASTM G22

2) measured by ASTM G21

Grade: 0 grade – Mold did not grow on a sample.

1 grade – Mold grew within 10% on a sample.

2 grade – Mold grew 10 to 30 % on a sample.

3 grade – Mold grew 30 to 60% on a sample.

4 grade – Mold grew 60% or more on a sample.

3) measured by ASTM D5589

<Example 5> Preparation of anti-microbial films using anti-microbial master batch

Anti-microbial packaging films were prepared by adding the anti-microbial master batch[1] of Example 3 respectively to LDPE and CPP in an amount of 5%. Anti-microbial tests were conducted by ASTM G22. As a control, common films to which the anti-microbial master batch was not added were used. The results are as described in Table 8.

[Table 8] Anti-microbial test for LDPE and CPP film

	E. coli (KCTC 1682)	S. typhimurium (KCTC 1925)	K. pneumoniae (KCTC 1621)
LDPE(common)	0mm	0mm	0mm
LDPE	6mm±1mm	11mm±1mm	9mm±1mm
CPP(common)	0mm	0mm	0mm

CPP	8mm±1mm	13mm±1mm	10mm±1mm

1) Composition 1 of Example 3: applied in LDPE, composition 3: applied in CPP

<Example 6> Preparation of anti-microbial plastic

Anti-microbial cutting boards with a size of 24cm x 40 cm were prepared by respectively adding 1 wt%, 3 wt%, and 5 wt% of the anti-microbial master batches of Composition 1 of Example 3 to high density polyethylene (HDPE) resin. Injection molding was conducted at 170 to 190 . In order to confirm durability of anti-microbial effects, after leaving the boards in flowing tap water for 30 days, anti-microbial effects before and after were compared. Results are as described in Table 9.

[Table 9] Anti-microbial test for anti-microbial plastic[1)]

	1 wt% add		3 wt% add		5 wt% add	
	initial	After 30 days	initial	After 30 days	initial	After 30 days
E. coli (KCTC 1682)	2.5mm±1 mm	2.0mm±1 mm	5.5mm±1 mm	5.0mm±1 mm	5.2mm±1 mm	5.1mm±1 mm
S. typhimurium (KCTC 1925)	3.5mm±1 mm	3.0mm±1 mm	7.0mm±1 mm	6.5mm±1 mm	7.5mm±1 mm	7.2mm±1 mm

1) ASTM G22 method

<Example 7> Preparation I of medical anti-microbial polymer resin

Medical anti-microbial master batches of solid pellet type were prepared by each adding 0.3 wt% of ciprofloxacin as the anti-microbial, to polyurethane (PU) resin, polyvinylchloride (PVC), silicon resin, which are commonly used

medical polymer resins. In order to confirm an anti-microbial effect, anti-microbial test was performed by ASTM G22 and results of inhibition zone are as described in Table 10.

[Table 10] Anti-microbial test for medical anti-microbial polymer resin

	polyurethane	polyvinylchloride	Silicon resin
E. coli (KCTC 1682)	4mm±0.1mm	6mm±0.1mm	3mm±0.1mm
E. coli (KCTC 2427)	3mm±0.1mm	4mm±0.1mm	1mm±0.1mm
S. aureus (KCTC 1621)	1mm±0.1mm	2.5mm±0.1mm	1.5mm±0.1mm
S. aureus (KCTC 1916)	2mm±0.1mm	3mm±0.1mm	2mm±0.1mm
S. typhimurium (KCTC 1925)	7mm±0.1mm	8mm±0.1mm	3mm±0.1mm
B. subtilis (KCTC 1021)	2mm±0.1mm	2mm±0.1mm	1.5mm±0.1mm
K. pneumoniae (KCTC 2690)	7mm±0.1mm	9mm±0.1mm	10mm±0.1mm

<Example 8> Preparation II of anti-microbial foly catheters and anti-microbial test

Anti-microbial foly catheters in the form of tubes were prepared by roll mixing a silicon resin, ciprofloxacin, and a catalyst with the composition of Table 11 for 30 to 60 minutes in an extrusion molding apparatus. Molding was conducted at 450 to 600 ℃/5 sec. The molded products were cured for 2 hours while maintaining them at 200 ℃ in a drier to remove remaining solvent. Anti-microbial test results are as described in Table 12. Anti-microbial effects were measured by ASTM G22 (measuring inhibited circle(zone)).

[Table 11] Compositions of anti-microbial foly catheters

	Peroxide catalyst	Pt catalyst	ciprofloxacin	Silicon resin	Total (wt%)
Composition 1	-	0.2	0.3	99.5	100
Composition 2	0.2	-	0.1	99.7	100
Composition 3	0.2	-	0.3	99.5	100
Composition 4	0.2	-	1.0	98.8	100
Composition 5	0.2	-	3.0	96.8	100
Composition 6	0.2	-	5.0	94.8	100

[Table 12] Anti-microbial test for anti-microbial foly catheters

	S. aureus (AATC 1621)	E.coli (AATC 1682)	P. aeruginosa (AATC 2004)
Composition 16	2.0±0.1mm	0.5±0.1mm	1.0±0.1mm
Composition 17	2.0±0.1mm	0.5±0.1mm	1.0±0.1mm
Composition 18	2.0±0.1mm	2.0±0.1mm	1.5±0.1mm
Composition 19	6.0±0.1mm	7.5±0.1mm	6.5±0.1mm
Composition 20	14.0±0.1mm	10.0±0.1mm	7.5±0.1mm
Composition 21	14.0±0.1mm	10.5±0.1mm	7.5±0.1mm

<Example 9> Preparation III of medical anti-microbial polymer resin and anti-microbial test

Anti-microbial prosthetic feet were prepared by roll mixing silicon resin and ciprofloxacin with the compositions of Table 13 respectively for 2 hours, introducing it into a mold to reflux for 1 hour while maintaining it at 160□, and then cooling to room temperature. Anti-microbial performance was examined by

measuring the bacteria decrease rate using the shake flask method. Results are as described in Table 14 and Table 15.

[Table 13] Compositions of anti-microbial prosthetic feet

	ciprofloxacin	Silicon resin	Total (wt%)
Composition 1	0.1	99.9	100
Composition 2	0.3	99.7	100
Composition 3	0.5	99.5	100
Composition 4	1.0	99.0	100

[Table 14] Anti-microbial test for anti-microbial prosthetic feet

	S. aureus (AATC 1621)	P. aeruginosa (AATC 2004)
Composition 1	1.0±1mm	3.5±1mm
Composition 2	7.0±1mm	12.0±1mm
Composition 3	9.0±1mm	14.0±1mm
Composition 4	9.0±1mm	15.0±1mm

[Table 15] Anti-microbial test for anti-microbial silicon prosthetic feet[1)]

		Number of bacteria		
		Immediately after inoculation	After 24 hours	Decrease rate (%)
S. aureus (ATCC 6538)	Blank	5.0×10^5	683×10^9	-
	composition 1	5.0×10^5	0	100
	composition 2	5.0×10^5	0	100
	composition 3	5.0×10^5	0	100
	composition 4	5.0×10^5	0	100

P. aeruginosa (ATCC27853)	Blank	5.0×10^5	1.72×10^{10}	-
	composition 1	5.0×10^5	6.0×10^2	99.99
	composition 2	5.0×10^5	0	100
	composition 3	5.0×10^5	0	100
	composition 4	5.0×10^5	0	100

1) Shake flask method conditions:

Test bacterial fluid was shaken at 25 for 24 hr, the number of times for shaken: 150 times/min.

2) Bacteria decrease rate was measured by the following Equation 1.

Decrease rate = (number of bacteria in blank after 24 hours – number of bacteria in sample after 24 hours)/ (number of bacteria in blank after 24 hours) x 100

【EFFECTS OF THE INVENTION】

The present invention applies anti-microbial materials, that are safe to a human body and has superior combination property with a common polymer resin, to common polymer resin and medical polymer resin, so as to maintain a superior anti-microbial effect even after molding, and solve a toxic problem by elution. Therefore, the present invention can provide the polymer resin composition, which is imparted an anti-microbial property to industrial appliances, household appliances, petrochemicals such as an anti-polluting paint, and natural rubber, as well as to medical materials.

【SCOPES OF PATENT CLAIM】

【CLAIM 1】

The anti-microbial polymer resin composition comprising at least one material selected from a group consisting of an anti-microbial agent selected from a group consisting of ciprofloxacin, grepafloxacin, lemefloxacin, norfloxacin, pipemidic acid, sparfloxacin, temafloxacin and tosufloxacin; and an anti-fungal/ anti-pollutant agent selected from a group consisting of ketoconazole, fluconazole, itraconazole, econazole, miconazole, iconazole as effective components.

【CLAIM 2】

The anti-microbial polymer resin composition according to claim 1, which comprises at least one the liquid-phase resin selected from a group consisting of alkyd resin, acryl resin, urethane resin, epoxy resin, phenol resin, urea resin, melamine resin, and a modified resin thereof, hydroxypropylacrylate, 1,6-hexanedioldiacrylate, pentaerythritoltriacrylate, and polyethylenedipentaerythritol as the polymer resin.

【CLAIM 3】

The anti-microbial polymer resin composition according to claim 1, which comprises at least one the solid polymer resin selected from a group consisting of Linear low density polyethylene(LLDPE), low density polyethylene(LDPE), high density polyethylene(HDPE), polypropylene (PP), polyvinylchloride (PVC), ABS(acrylonitrile-butadiene-styrene), SAN(Styrene Acrylonitrile), polycarbonate (PC), polystyrene (PS), polyvinylalcohol (PVA), polyacrylonitrile, polybutadiene, polyacrylic acid, polyacrylimide, polysulfone, polyacetal, polyamide-imide, polytetrafluoroethylene, polyneoprene, polydimethylsiloxane, polymethylmethacrylate, polyetheretherketone,

polyphenylenesulfide, polyvinylfluoride, polyvinylacetate, polyetherimide, polyvinylidinefluoride, polyethersulfone and polyurethane as the polymer resin.

【CLAIM 4】

The anti-microbial polymer resin composition according to claim 1, wherein the anti-microbial polymer resin composition is composed of the master batch form.

【CLAIM 5】

The anti-microbial polymer resin composition according to claim 1, wherein the anti-microbial agent is contained in an amount of 0.1 to 30 wt% of the total composition.

【CLAIM 6】

The anti-microbial polymer resin composition according to claim 1, wherein the anti-fungal/ anti-pollutant agent is contained in an amount of 0.1 to 30 wt% of the total composition.

【CLAIM 7】

The anti-microbial plastic composition adding the resin composition of the anti-microbial master batch type according to claim 4 of 0.1 to 30 wt%.

【CLAIM 8】

The anti-microbial polymer resin composition according to claim 1, wherein the resin composition is a medical polymer resin.

【CLAIM 9】

The anti-microbial polymer resin composition according to claim 8, wherein the medical polymer resin is selected from a group consisting of polyethylene (PE), polypropylene (PP), polycarbonate (PC), polyvinylchloride (PVC), polystyrene (PS), epoxy resin, polytetrafluoroethylene (PTFE), polyacetal (POM), polyamide (PA), polyurethane (PU), ethylene-vinylacetate copolymer

(EVA), polymethylmethacrylate (PMMA), polyvinylalcohol (PVA), polycaprolactone (PCL), and a copolymer thereof; silicon resin; natural rubber; and a synthetic rubber.